740116-556

3/PRTS

10/519555
DT01 Rec'd PCT/PTC 28 DEC 2004

Membrane separation process for the enrichment of at least one gas component in a gas flow

The invention firstly concerns a membrane separation process for the enrichment of at least one gas component in a gas flow, particularly for the oxygen enrichment of the air and/or for the enrichment of carbon dioxide in a gas flow. The gas flow supposed to the enrichment of the gas is led to a membrane separation unit including at least one membrane. This is where takes place the separation of the gas flow into a retentate, which is discharged on the retentate side of the membrane, and a permeate, which is discharged on the permeate side of the membrane. Secondly, this invention refers to a membrane-separation plant for the enrichment of at least one gas component in a gas flow, particularly for the oxygen enrichment of air. It provides at least one membrane separation device including at least one membrane, with the gas flow supposed to the enrichment of the gas being led to a membrane separation unit. The separation of the gas flow into a retentate, which is discharged on the retentate side of the membrane, and a permeate, which is discharged on the permeate side of the membrane, takes place on the membrane.

Today oxygen and nitrogen are mainly generated by means of the cryogenic separation developed by Linde and Claude 100 years ago (Air Liquide), which presupposes that air is cooled down to –180°C and then distilled and/or rectified. Because of the extreme low temperatures energy consumption costs are inevitably high. The separation device industry concerned with the separation of technical gas are extremely expensive because of their complex form and arrangement. They are used for the production of pure gases in large volumes.

Further possibilities to produce oxygen-enriched air are the methods of adsorptive decomposition into nitrogen and oxygen using the molecular sieve, zeolites and activated charcoal. Separation takes place according to the size of molecules, as well as to the adsorptive- and diffuse interactions. The disadvantages of the aforesaid method are high energy consumption and expensive equipment. The plants are usually built for the industry with the purpose to provide with high productivity, primarily for the pure gases. Because of the complexity of the components the costs for investment, capital and maintenance are very high.

In comparison to the existing gas separation methods the gas separation by membrane is remarkable for its low technical expense. Speaking about the membranous gas separation, it is relevant to distinguish, according to the aggregative state, "fluid" or " gaseous" and, according to the mediums or components to separate gas-membrane contactor, membranous pervaporation and gas permeation. The methods using the gas-membrane contactors are characterized by the fluid phase on the permeate side of the membrane, where the permeate is absorbed and the chemical reaction takes place. The gas pervaporation is a method for the separation of organic water solutions or of organic fluids, allowing the permeated components to go from the liquid state into the vaporized state. The distinguishing feature of the gas permeation is that both the feed stream respectively the retentate stream as well as the permeate stream are in gaseous state.

The advantage of the gas separation by means of membranes is the low-energy generation of gas of the desired quality. The costs for providing the device as well as for maintenance and service are considerably lower compared to the classical separation methods. Furthermore, the control and regulation expenses for the present membrane separation process are low. The facilities are often modularly built and enable the precise adjustment and regulation of the necessary volume streams. Another advantage is the efficiency of the equipment and the specific lifespan of the single components. One disadvantage of the existing methods for membrane separation is that the gas must be led to the membrane separation unit under high pressure to allow the permeation of the component to be separated respectively enriched to pass into the permeate stream. The compression of the input gas flow before entering the membrane separation unit involves considerable energy consumption and is therefore very expensive.

The task of the present invention is to create a membrane separation process and a separation plant as mentioned above, which would allow the gas separation and/or enrichment of a gas component in the gas flow involving low energy consumption and low capital and production costs.

Before entering the membrane separation unit, the gas flow is compressed up to the inlet pressure, which is higher than the surrounding pressure. At the permeate side the pressure is lowered compared with the inlet pressure. The membrane separation process provides an alternative for the solution of the problem mentioned above, which consists firstly in reducing the pressure of the gas flow in the membrane separation unit, secondly to reducing the outlet pressure of the retentate stream to below the pressure found in the sourrounding. Thirdly, The pressure of the retentate stream on the permeate side is reduced compared to the pressure of the original pressure. The task mentioned above is solved involving at least one vacuuming compressor for lowering the pressure on the permeate side of the membrane, particularly to below 1 bar.

The main idea of the invention is to reduce the pressure on the permeate side of the membrane compared to the inlet pressure of the gas component. The power needed to pass through the membrane is determined by the difference of pressure between the feed stream and the permeate stream respectively through the difference of pressure between the retentate stream and the downstream. Using the technology of the existing method of membrane separation the feed stream must be compressed to a high level – usually between 8 and 20 bar, and thus providing a rather high driving force. Our invention avoids these technologies. The driving force needed to allow the gas components to pass through the membrane into the permeate stream is produced not by means of compression of the input gas flow, but by lowering the pressure on the permeate side. Since the energy needed for the compression of a gas flow respectively for lowering the pressure is proportional to the gas volume, it is possible to use this method for reducing the energy consumption for the enrichment of a gas component in a gas flow compared. There is no need to compress the whole feed gas stream, but it is sufficient to lower the pressure of the permeate stream that is usually much lower than the input gas flow. It is the membranous separation method that first enables to discover new application and practice fields and to apply the membranous separation method efficiently in certain fields.

There are two alternative forms of the membrane separation method. On the one hand, the gas flow can be compressed up to the inlet pressure above the ambient pressure before it enters the membrane separation unit. In this case, the pressure level on the retentate side of the membrane can be reduced, whereas the gas flow is led up to the membrane separation device under the ambient pressure. On the other hand, it is necessary to reduce the pressure on the permeate side of the membrane compared to the outlet pressure of the retentate stream, so that the gas components can pass through the membrane.

The important thing is that the compression of the gas flow before entering the membrane separation unit respectively the lowering of the pressure of the retentate stream is exactly at the level needed to compensate the loss of pressure that occurs when the gas flow is passing to the retentate side of the membrane separation unit. The lower the gas flow is compressed respectively the smaller the outlet pressure of the retentate stream is lowered below the ambient pressure, the less energy consumption is connected to the membrane separation process. At the same time the capital and production expenses are reduced.

In addition, it is very important that the pressure level on the permeate side must be strongly reduced to ensure a sufficient driving force for the enrichment of the gas components in the downstream. It is clear according to the invention that in addition to lowering the pressure on the permeate side, the pressure of the input gas flow can be increased, which includes of rise in driving force.

Even if the invented method is used particularly for oxygen enrichment of the air, it is certainly possible to enrich other gas components in a gas flow. For example, the invention can be used for nitrogen enrichment of the air, involving the oxygen passing through the membrane into the permeate stream and at the same time the retentate stream being enriched with nitrogen. Hence the invented method can be used both for the separation of carbon dioxide and for the separation and / or enrichment of fuel gas. Finally it is also possible to imply the present method not only for the enrichment of the gas components in a gas flow, but also for the enrichment of components in any fluid medium.

The enrichment of a gas component in a gas flow is based on the mechanism of gas permeation. The input gas flow or the retentate stream and the permeate stream are in a gaseous state. This process can be described as the solubility-diffusion-mechanism. The sorption of the permeated component of the gas flow, for example of the oxygen in the air, takes place on the membrane surface in the membrane separation unit. It results in the diffusion through the membrane-separating layer and finally in the desorption on the permeate side of the membrane.

One main application field of the invented method is the oxygen enrichment of the air. The enriched air can be used in various areas. The present method provides a means for lowering the energy costs and is therefore an efficient method for the oxygen enrichment of the air. A pressure relieve at the permeate side of the membrane promotes the improvement of the separating process. The oxygen in the permeate rises as a result of the increase of transmembranous pressure difference.

At the same time the volume stream of the permeate stream increases. Both these effects lead to the improvement of separation quality. Hence the method enables to control the volume stream of the permeate by using a simple and an efficient technology.

On the basis of the gas permeation mechanism the separation of the input stream (feed stream) into an oxygen-enriched permeate stream and an oxygen-depleted retentate stream takes place. With the help of the method it is now possible to reach a concentration of oxygen in the permeate stream above 22-45 vol.%, with an oxygen concentration of the permeate stream of about 30 vol.%. It is basically possible that the gas component can be found in the retentate stream. In this case a majority respectively many of the components pass through the membrane into the downstream, while the components object to the enrichment do not pass through the membrane and are enriched in the retentate stream.

Due to the method it becomes possible to regulate the volume stream of the permeate stream and/or the concentration of the components subject to enrich in the permeate stream by relieving the pressure on the side of the membrane. In this connection there is a possibility of directing the volume stream of the permeate stream and/or the concentration of the components object to the enrichment exactly according to user-related requirements at a low energy consumption level.

An advantageous constructive form of the invention represents a single-stage method. "Single-stage" concerns the increase of pressure of the feed stream or the decrease of pressure of the retentate and/ or the foreseen pressure relieve of the permeate. The single-stage method is remarkable for its simple structure and allows to carry out the process distinctly. The single-stage implementation of the method is most productive in technical conditions, when it is necessary to get a partly enriched permeate. It refers, for example, to the oxygen enrichment of the air. The single-stage implementation of the method leads to lower productive and capital expenses and is therefore very efficient.

To keep the energy consumption for the compression of the gas flow on a low level before it enters into the membrane separation unit, it is preferable that the pressure difference between the gas flow and the retentate stream approximately amounts to 1 bar, more preferable 0,2- 0,5 bar. In this connection it is vital that the pressure difference between the retentate and the permeate stream is enough to compensate the pressure loss occurring on the retentate side when blowing through the membrane separation unit. If the difference is not enough, the concentration of the components of the permeate stream becomes more sparse.

According to another advantageous form of implementation the invention suggests that the difference of pressure should be adjusted depending on the concentration of the component subject to enrichment in the permeate stream. Generally it is considered, that the pressure level of the feed stream and that of the retentate modulated corresponding to adjusted concentrations in the permeate stream should be as little as possible, in order to minimize the energy consumption.

The invention showed further: Firstly, the permeate stream should be discharged under the absolute pressure ranging from 0,2 to 2,0 bar, that of 0,4 till 1,4 bar being rather preferable. Secondly, the discharge under absolute pressure between 0,5 and 1 bar and especially under less than 1 bar, i.e. under the under-pressure index, is to enable the enriched gas component to pass through the membrane in the permeate stream while concomitant factors for energy consumption are on an low level. Thirdly, the preferable pressure level ranges between the 0,5 and 0,65 bar. The supplied gas flow should have the absolute pressure of 1 to 6 bar, with the pressure of less than 3 bar and especially that of between 1,35 and 1,5 bar being of advantage, so that the difference of pressure between the feed and the permeate stream should be set between 0,2 and 0,5 bar. The retentate stream characterized by the absolute pressure levels ranging between 1 and 5,5 bar, with preference of 2,5 and especially of 1 bar, i.e. of its environmental pressure, is easily dischargeable. It should be noted that all the values from the afore-named value circle are regarded here according to the present invention. However, when applying the invention, one must remember that every value chosen from the value circle may acquire specific advantages.

The invention presupposes that e.g. plate-modules, pocket modules or hollow fiber modules can be used as membrane separation devices. Sure, one can also engage a complex of different separation units, in order to reach the best possible results of separation. The physical properties of the membranes, such as e.g. separation layer thickness of the membranes, permeability, selectivity and durability under high temperatures, influence the capacity of the membrane separation unit. Depending on the given case of implementation, it is possible to any membrane type.

Due to the absence of moving components the membrane separation unit works at the mechanical no-load principle and, therefore, has non-restricted durability. Consequently, the method itself is very thrifty in maintenance. The influence of membrane type deterioration is of a secondary interest in every particular case.

In order to produce different volume streams, it is presupposed to divide the gas flow in at least two partial streams and treat it by a set of parallel working membrane separation devices and / or membrane separation units. It goes without saying that it is also possible to use several modules at the same time, which are incorporated into a membrane separation unit. Yet it is also possible to use a number of membrane separation devices in a cascade connection.

To avoid damages of the membrane separation unit, respectively membrane, and/or pre- or after-compression, respectively the vacuuming compression of gases, it is required to clear off the waste components such as particle and/or oils and/or fats. The penetration of such wastes in the device components should be avoided, because these wastes may have negative affects on the separation respectively concentration of the gas component. The membrane should be handled with extra care. However it is important to minimize the expenditures for the gas cleaning, in order to keep the costs at a low level.

It is possible to cool off or to warm the gas flow, preferably after it has been compressed, before it enters the membrane separation unit. The temperatures can

be controlled by the given membrane type. While warming up the gas flow it is possible to prevent the condensation of the gas components, such as e.g. water steam. The gas flow of 35°C to 50°C, preferably that of 45°C, is warmed up to 50°C to 75°C, with preference to 60°C to 65°C. The cooling off presupposes temperatures between 0°C to 30°C and especially 0°C to 20°C. The warming up or cooling of the gas flow can be undertaken respectively of the membrane type, depending on the temperature of specific features, which determine the membranous separation process. If the invented technique is aimed at the concentration of oxygen in the atmosphere, the air may be supplied directly to the membrane separation unit and the process may take place under ambient temperatures.

It is especially preferred to cultivate high concentrations of oxygen in the air with the help of the described process in order to apply the received permeate substance for gas-motor firing of the landfill gases. After the technical instruction on the recycling of the domestic wastes was introduced, the gas quality rates for the landfill gas have considerably changed. The diffusive extraction of methane from the landfill side is diminished by special precautions of the landfill techniques, gas drainages and complex pipes. The gas quality may differ and can be used in the gas engines of the co-generation power plants only with the methane concentration of no less than 40 % of the landfill gas content. There is an alternative for the methane to be fired or evaporated into the atmosphere, the latter being destructive to the environment. The methane is 23 times as harmful as carbon dioxide by coursing the greenhouse effect. Not using it means wasting a precious energy source.

The law on the alternative energy sources (EEG) ensures fixed operating revenues for power generation of landfill gas. The systems engineering of the landfill is still existing, but often it cannot be applied because of the low quality of the gas.

The single-stage process of the oxygen enrichment of the air makes it possible to create equipment modules for combustion air with a higher content of oxygen.

The economic basis of the process enables the air to be further used with the gases of lower quality (containing less than 40% of methane) for firing in the block thermal power plants. As a result, large quantities of the inert gases are replaced and one gets the inflammable air-mixtures, which successfully provide the functioning of engines. Other advantages are as follows: the reduction of emissions, better effects and efficiency of the fuel qualities. Besides the economic aspect, the crucial importance lies on the contributing to saving the environment.

The technique described above allows to be applied in the case of wood gases or special gases such as sevage gas or biogas, without determining any special conditions for them. Otherwise it is possible to use the technique in micro turbine and fuel cell technologies. Therefore, it is possible to improve the effects by using the technology described above.

Moreover, it is possible to apply the technique described above with corresponding modifications of the process in sporting centers, particularly in the health spas. The

air in sport clubs or health spas is known to undergo processes of enrichment or reduction of oxygen content in order to control the sport activity of the people or to promote the progress of sportsmen and to keep them in good health. Oxygen used with this purpose usually comes from the special compressed-gas tanks. This can be considered to be highly expensive. The technique described above is therefore advantageous in this case, in so far as it does not require much energy and as it is economic. Therefore, it is relevant to speak about the possibility of applying the technique to the sphere of climate modifications. One can also use the technique for oxygen enrichment of the sewage in the aerotanks of the purification equipment, where one can balance too little or unstable oxygen content. And at last, it is possible to use the technique in the chemical processes, such as e.g. in the blast furnaces sphere, what will considerably diminish the costs.

The example describes the invention further, without restricting the creativity of thought. The drafts illustrate the following:

Detail 1 shows a manufacturing scheme of the oxygen enrichment of the air using a membrane separation unit and

Detail 2 shows the curve of the oxygen concentration in the permeate stream in dependence on the power needed to enrich the permeate stream and on the volume stream of the permeate.

Detail 1 represents a one-stage method of oxygen enrichment of the air with the help of the membrane separation system 1. According to detail 1 the membrane separation system includes a membrane separation unit 2, a vacuuming compressor 3, that is switched on before the membrane separation unit 2 and e.g. could be represented by a compressor, a compressor 4, as well as the heat exchanger 5 and filter 6, which are switched on before the membrane separation unit.

The air 7 subject to enrichment is evacuated directly from the atmosphere and supplied to the filter, in order to be cleaned of the dust corpuscles or any other rough pollution. Further the air 7 comes to the compressor 4, where it is compressed up to the absolute pressure level of 1 to 3 bar, particularly to a level of approximately 1,5 bar.

After the compression of the air 7, it is supplied to the heat exchanger, where it is either warmed up or cooled off. This procedure helps to determine the tolerable temperatures of the membrane separation unit, in particular the tolerability of the membrane used in the membrane separation device 10. On the other hand, the warming up of the air 7 helps to avoid the condensation of the water steam, supplied to the filter together with the air 7.

The air, passed through the heat exchanger 5, is supplied to the membrane separation unit 2 and is divided into an oxygen-depleted retentate 8 and an oxygen-enriched permeate 9.

The vacuuming compressor 3 comes to a fore to decrease the pressure level on the permeate side 11 of the membrane separation unit 2. It is preferable to decrease the pressure level on the permeate side 11 of the membrane separation unit 2 down to 0,4 bar to maximum 1,4 bar, where that of less than 1 bar is of advantage. At the same time the pressure on the retentate side 12 of the membrane separation unit should make up 1 to 2,5 bar, in particular 1 bar.

The membrane separation unit 2 may consist of membrane separation devices 10 which may differ structurally. One can use plate modules, pocket modules or/and hollow fiber modules as membrane separation devices 10. There are also potentialities to utilize other constructions of the membrane separation devices. The membrane separation devices can be used concurrently to produce different volume streams. However it is vitally important that the membrane separation device 10 must include at least one membrane, which would enable the penetration of the selected gas components into the permeate 9.

A considerable advantage of this method is that it is carried out on one level and is therefore easy to use. The division of the air volume stream 7, supplied to the membrane separation unit, is based on the principle of gas permeation. The driving force of this division is the difference of pressure between the air 7 and the permeate 9. It is possible to manage the level of gas enrichment with any of its components by means of modifying volume streams of gases, e.g. of the air 7, of the retentate 8 and of the permeate 9 as well as by pressure level control in every particular case. The pressure on the permeate side 11 of the membrane separation unit 2 adjusted between 0,4 and 1,4 bar with under-pressure indexes being preferred, has a positive impact on the process of division. In this way it is possible to regulate the volume stream and the oxygen content of the permeate 9.

The invention determines that the difference of pressure between the air 7 supplied into the membrane separation unit 2, and the oxygen-depleted retentate 8 should not exceed 0,8 bar. The difference can be regulated to save power and to produce the permeate 9 with the needed oxygen concentration.

However, it is not shown in the details that the compressor 4 may be adjusted on the retentate side 12 of the membrane in a way, that the retentate 8 will be absorbed. In this case the air 7 must not be compressed before entering the membrane separation unit 2. In this case the driving force of the division as well as enrichment of the permeate 9 with oxygen are defined by the difference of pressure between the retentate 8 and the permeate 9.

In order to enable an easy transportation of the separation device, it is further asserted that all its components, including the membrane separation unit 2, vacuuming compressor 3, compressor 4 as well as the other elements, which belong to the membrane separation system, should be mobile. It is especially important as the separation plant has a compact structure and consequently is small in size and offers component control units easy to control.

An embodiment of the oxygen enrichment of the air 7 presupposes that the air 7 is led up to the membrane separation unit 2 in a volume stream of 7.6 m^3/h under the absolute pressure of 1.3 bar. In the membrane separation unit 2 the air stream 7 is separated into an oxygen-enriched volume stream, the permeate 9, and an oxygen-depleted volume stream, the retentate 8. The pressure on the permeate side is eased with the help of the vacuuming compressor 3 down to 200 mbar. The result is a volume stream of 3.1 m^3/h under the absolute pressure of 0.8 bar with the oxygen content of 25.46%. On the retentate side 12 the pressure reaches an absolute level of 1.15 bar. The volume stream of retentate 8 with oxygen content of 18.75% constitutes 4.5 m^3/h.

The detail 2 shows a scheme of the qualitative change of the content of oxygen (curve b) y_{O2} [%], depending on decrease of pressure on the permeate side of the membrane separation unit.

In the course of invention it was found out that the optimum for the oxygen enriched volume stream on the permeate side occurs depending on the pressure level of the feed stream and the retentate. It leads to the increase of oxygen concentration on the permeate side. If the difference of pressure between the feed stream and the retentate stream is too small, the reached oxygen concentration decreases.

Moreover, in the course of the invention it was found out that the ease of pressure on the permeate side compared to the inlet pressure of the feed stream results in a better and higher concentration of the enriched component in the permeate stream.

The volume stream V_p [m^3/h] of the permeate shows a degressive rising curve with the sinking pressure level on the permeate side (curve a). On the contrary, the energy consumption P_{el} [kW] needed to ease the pressure level on the permeate side, which is shown on the detail 2 by the curve c, rises progressively with the growing pressure ease of the permeate stream.

In addition, we want to point out that the recycling of the permeate 9 and/or the retentate 8 is basically possible, although it is not foreseen. Furthermore, the inverse coupling of the permeate 9 with the retentate 8 is also basically possible, although not foreseen. This is mostly applied when the implementation of the invented method for the oxygen enrichment is concerned.